

## Actinides in Alkaline Media: Dissolution, Mineral Associations, and Speciation in Hanford Waste Tank Sludge Simulants

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We have investigated the leaching behavior of actinides from simulants of tank waste sludges derived from the BiPO<sub>4</sub>, Redox, and PUREX processes, the principal chemical separations processes that operated at the Hanford site during 40+ years of plutonium production. Fundamental investigations of the speciation of uranium and neptunium in solutions representative of proposed alkaline sludge washing liquors have also been completed. Correlation of the results from sludge leaching indicate that, while Am and Pu are generally not appreciably dissolved from the sludges into alkaline solutions in the absence of oxidants, Np and U can be mobilized during alkaline sludge washing. Leaching of sludges with acidic solutions and strong complexing agents indicate considerable association of all actinide ions with Cr, Fe, and Mn oxides in the sludge simulants. Electrochemical experiments conducted in strongly alkaline solutions have defined the formal potentials of Np in strong base and reveal that mononuclear hydrolysis products dominate the speciation of neptunium (and by analogy U and Pu) in concentrated alkali. The results of these observations are discussed in the context of alkaline sludge washing procedures associated with waste tank remediation.

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### I. Introduction:

During 40+ years of operations at the Hanford Site, a total of 177 underground tanks were built for storage of the radioactive byproducts of plutonium production. At shutdown, the 149 single-shell tanks contained  $1.4 \times 10^5$  m<sup>3</sup> of (mostly) solid and liquid wastes and  $1.7 \times 10^8$  curies of radioactive materials including <sup>90</sup>Sr, <sup>137</sup>Cs, <sup>99</sup>Tc, and transuranium elements (TRU's)<sup>1</sup>. The 28 double-shell tanks contain about  $9 \times 10^4$  m<sup>3</sup> and about  $9.0 \times 10^7$  curies of similar materials. Site closure plans require that these materials be removed from the tanks with the radioactive materials sent to geologic storage in a mined repository.

Over the history of operations at Hanford, three principal chemical separations processes were operated for plutonium separation (bismuth phosphate, REDOX, and PUREX processes). Though initially wastes from various process streams were segregated, limited capacity of storage

space ultimately led to the mixing of combinations of organic and inorganic reagents (and reaction byproducts) from different processes. The wastes were mixed tank-to-tank to take best advantage of available tank storage space, and, as required, processed through evaporators to reduce their water content to conserve precious tank storage space. Most of the fission products, the U and Pu incompletely recovered during chemical processing, and most of the neptunium and transplutonium elements generated during plutonium production remain in the tanks.

With time, the wastes in most of these tanks stratified to produce a clay-like bottom sludge, an intermediate solution/slurry phase, and an overlying salt cake. The long-lived radionuclides are distributed among these phases, though the TRU's and Sr are most concentrated in the sludge phase. Those tanks containing appreciable amounts of chelating agents have the actinides more widely distributed among the various tank waste phases.

The tank waste cleanup plan calls for the stratified contents of the tanks to be pumped or sluiced out,

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fractionated to segregate as many of the radioactive and nonradioactive components as is practical, and finally converted to suitable solid materials for disposal. At present, the last stage of removal prior to glass-making is slated to be a wash of the sludge layer with a concentrated caustic solution. The primary objective of sludge washing is to lower the Al, P, S, and Cr content of the sludge, as these elements interfere with the production of stable glass logs or increase the susceptibility of the glass to degradation. It is intended in this processing protocol that the transuranics will remain in the sludge and be directly converted to glass.

Our research seeks to increase understanding of the chemistry of actinides during alkaline scrubs of tank waste sludges. In the following, selected results of sludge simulant leaching experiments and of actinide speciation in strongly alkaline solutions are discussed.

## II. Sludge Leaching Procedures

We have investigated the leaching behavior of U, Np, Pu, and Am from sludge simulants prepared according to standard methods <sup>2)</sup>. The simulants of sludges from the BiPO<sub>4</sub>, Redox, and PUREX processes vary substantially in composition. Details of the elemental analysis of the synthesized sludges has been reported in an earlier publication <sup>3)</sup>. The Cycle 3 BiPO<sub>4</sub> sludge is about 36% by weight BiPO<sub>4</sub>. This sample also contains about 11% lanthanide (from LaF<sub>3</sub> precipitation) and the highest concentration of manganese (7%) and Cr (5%) of the three sludge types. The Redox sludge is 24% Al and contains 4% Cr, 5% Fe, and 1% Mn. The PUREX sludge is highest in Fe (24%) but also contains 7% Al and 2% Mn but no Cr.

In most cases, leaching of the sludges was done in series using increasingly aggressive solutions, in the sequence:

- 1) 0.01 M NaNO<sub>2</sub> + 0.01 M NaOH (sluicing liquid from Hanford baseline strategy)
- 2) 3.0 M NaOH (leachant from Hanford baseline strategy)
- 3) H<sub>2</sub>O
- 4) 0.05 M Glycolic Acid + 0.10 M NaOH
- 5) 0.10 M HNO<sub>3</sub>
- 6) 2.0 M HNO<sub>3</sub>
- 7) 0.50 M 1-Hydroxyethane-1,1-diphosphonic acid (HEDPA)

Solutions 1-3 represent baseline sludge washing solutions. Solutions 4-7 are experimental solutions that were designed to determine how resistant to leaching the sludge components are and to teach us with which non-radioactive components the actinides associate. Some sludge washings were performed using parallel (rather than series) contacts with

these solutions. Alkaline sludge washing is designed to extract as much P, Cr, Al, and S from the sludges as possible, preferably without dissolving the actinides. Sludge leachates for the non-radioactive sludges were analyzed using spectrophotometry while Energy Dispersive Spectroscopy (EDS) profiled what remained in the sludge layer. Spectrophotometric analysis of sludge supernatants indicate that some, but not all, of the Cr(VI) is removed from those sludges containing Cr in the 3.0 M NaOH wash. We conducted ICP analysis for Al and found that only about 6% of the Al in the Redox sludge and 28% of the Al in the PUREX sludge are dissolved in 3.0 M NaOH (at room temperature). This result suggests that under the leaching conditions, a thermodynamic solubility limit may be controlling the amount of Al dissolved. The Al content of the BiPO<sub>4</sub> sludge is low.

The exploratory washes with more aggressive reagents demonstrate the substantial dissolution of Fe from both the PUREX and Redox sludges in 0.1 M HNO<sub>3</sub>. The 2.0 M HNO<sub>3</sub> wash apparently solubilizes more Fe, the lanthanides, and the reduced chromium species, presumed to be Cr<sub>2</sub>O<sub>3</sub>. The wash with HEDPA leads to dissolution of Mn. Aluminum analysis indicates 66% of the aluminum in the Redox and 21% of that in PUREX dissolves in 0.1 M HNO<sub>3</sub>; 6% of Redox, 22% of PUREX Al dissolves in 2.0 M HNO<sub>3</sub>; 10% of Redox, 32% of PUREX Al dissolves in HEDPA. The aluminum sludge washes describe parallel rather than consecutive contacts and so do not demonstrate the cumulative effect of the leachates. It is clear that a simple room temperature alkaline scrub is inadequate for Al removal.

### 1. Plutonium and Americium in Leachates

In the parallel experiments with sludges that were pre-equilibrated with the individual actinides, we observed only very small amounts of Pu (whether introduced to the sludge in the oxidized (Pu(VI)) or reduced (Pu(III/IV)) forms) and Am in the baseline sludge wash supernatants (leachates 1-3) from all of the sludges <sup>3)</sup>. In the exploratory washes, americium behaved exactly like the lanthanides, dissolving quantitatively in the 2.0 M HNO<sub>3</sub> leachate from each sludge simulant. Plutonium behavior is more complex. The 20-30% of either oxidized or reduced Pu that dissolved in 0.1 M HNO<sub>3</sub> coincides with the dissolution of about 66% of the aluminum from the REDOX sludge. Upon filtration, the Pu was removed from the sample, suggesting a high probability that the Pu is adsorbed on alumina colloids in this sample rather than in true solution. The 30-60% of Pu (oxidized and reduced) in the 2.0 M HNO<sub>3</sub> leachate of the modified BiPO<sub>4</sub> sludge is not radiocolloid, but truly in solution. Generally less than 10% of the radiotracer Pu was solubilized from

Redox and PUREX sludge simulants with only minor differences between Pu initially oxidized and reduced. Colorimetric analysis indicates substantial dissolution of  $\text{Fe}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  in these leachates. One possible implication of this result is that  $\text{PuO}_2(\text{s})$  may well be controlling Pu solubility (though these experiments were conducted using  $^{238}\text{Pu}$  tracer, for which the thermodynamic solubility limits would not necessarily be exceeded). Upon contact with the HEDPA chelating agent, somewhat larger amounts of oxidized Pu than reduced are dissolved. The colorimetric analysis indicates dissolution of  $\text{MnO}_2$  in this leachate.

Though leaching of americium from the sludges indicated little solubilization until the 2.0 M  $\text{HNO}_3$  leachate, oxidative leaching did have a measurable effect on Am dissolution. The leaching of Am was enhanced by  $\text{K}_2\text{S}_2\text{O}_8$  in 3 M NaOH at  $100^\circ\text{C}$ , though no enhancement was observed in 3 M NaOH at  $20^\circ\text{C}$ , or in the supernatant simulant ( $\text{Na}_2\text{CO}_3/\text{NaOH}/\text{NaNO}_3$ ) at  $100^\circ\text{C}$ . This result may indicate partial oxidation of Am(III) to Am(V). Such alterations in Am speciation will be a concern should oxidative leaching for enhanced Cr removal be pursued. It also implies a higher probability for solubilization of Pu and Np, both of which are easier to oxidize than Am.

## 2. Uranium and Neptunium in Leachates

Np leaching experiments were done using  $^{237}\text{Np}(\text{V})$  at radiotracer concentrations, while the uranium experiments were conducted using both radiotracer and macro concentrations of U(VI). In the baseline sludge washing process, 3.0 M NaOH removes about 25% of the radiotracer  $^{237}\text{Np}$  and 10-15 % of its  $^{233}\text{Pa}$  daughter. The Np appears to be in true solution, i.e., not in a filterable form. The dilute acid leach removes only a small amount of the Np from the Redox sludge, but none from any other samples. The 2.0 M  $\text{HNO}_3$  wash dissolved at least 50% of all of the Np from all sludge samples. The remaining 10-20% dissolved with the HEDPA wash. Not surprisingly (due to the substantial differences in their chemistries), the  $^{233}\text{Pa}$  daughter dissolved in the opposite pattern, i.e., more in the HEDPA than in the  $\text{HNO}_3$  leachate.

U(VI) was loaded onto the sludges at a tracer level using  $^{233}\text{U}$  or a macro level ( $^{238}\text{U}$ , 0.5% by weight in the sludge) from a solution of 0.10 M  $\text{Na}_2\text{CO}_3/0.50$  M NaOH/1.0 M  $\text{NaNO}_3$ . In addition, the Redox sludge contains about 0.45% (by weight)  $^{238}\text{U}$  that was incorporated into the sludge during the sludge preparation process. Sludge leaching for U samples was done in a parallel (rather than serial) fashion, as the serial washing left little material for the final washings. The leaching efficiencies of U by 0.01 M NaOH/0.01 M  $\text{NaNO}_3$ ,  $\text{H}_2\text{O}$ , and 0.1 M NaOH/0.05 M Glycolic acid were generally low from all four sludges. Less than 1% of U was

found in these leaching solutions from  $\text{BiPO}_4$  sludges. For PUREX and Redox sludges, the percentage of U in these leachates was up to 16% for PUREX and 24% for Redox sludges. These percentages correlate with the relative aluminum contents of these two sludges. The U was quantitatively dissolved in the HEDPA and 2.0 M  $\text{HNO}_3$  leachates, 30-60% dissolved in 0.1 M  $\text{HNO}_3$ . Generally speaking, the leaching efficiencies at tracer and macro levels are quite similar for all the four sludges. However, in the 3 M NaOH leaching from Redox and PUREX sludges 82%-89% of  $^{233}\text{U}$  (tracer only) was found in the leachate. In contrast, only ~ 15% of  $^{238}\text{U}$  (macro U experiment) was found in the same leachate (corresponding to  $\sim 2 \cdot 10^{-5}$  M U in 3 M NaOH). This difference suggests that different mechanisms may be involved in the leaching at tracer and macro levels. We believe that sorption/desorption onto mineral surfaces was probably the process at the tracer level, while precipitation/dissolution was the process at the macro level. Radiolysis and drying of sludges had little impact on uranium dissolution during sludge washing.

## III. Uranium Species in Sludge Simulants

It is generally considered that the oxides/hydroxides will control actinide solubility in alkaline media. To test whether this is true for the the sludge simulants, we conducted EXAFS experiments on U(VI) in each of the four sludges. Due to the interference of certain lanthanides in the sludges on the U  $L_{\text{III}}$  edge spectra, the EXAFS were collected at U  $L_{\text{II}}$  edge. The Fourier Transforms of the EXAFS spectra are shown in Figure 1. The data for a reference material (uranyl phosphate) are also included for comparison.

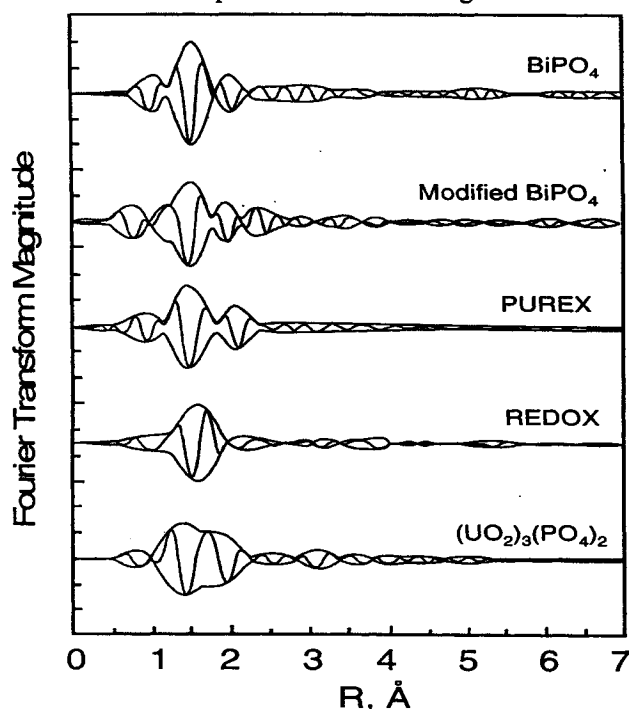
Though these data are quite preliminary, two observations can be made. 1) The chemical environments of U(VI) in the four sludge simulants are different. Only the spectrum for the REDOX sludge is similar to that of the uranyl hydroxide. This implies that U(VI) is probably incorporated into the two  $\text{BiPO}_4$  sludges and the PUREX sludge rather than being precipitated as hydrolysis products on the surface. 2) No evidence was found for the coordination of U(VI) with phosphate in the two  $\text{BiPO}_4$  sludges. Further studies on the characterization with EXAFS have been planned.

## IV. Neptunium Speciation in Concentrated Alkali

The sludge leaching experiments teach us that, although we cannot ignore plutonium solubilization during alkaline sludge washing, it is most important to profile the speciation of the hexavalent and pentavalent actinide ions in the solution phase. The most stable species representing

these oxidation states are U(VI) and Np(V). We therefore elected to concentrate our first speciation efforts on these metals. The Np investigation employed UV-Visible-Near IR spectrophotometry, radiochemistry, and electrochemistry as the principal analytical methods. Through a combination of observations, we have established that at base concentrations above 1.0 M the nearly isostructural ions  $\text{NpO}_2(\text{OH})_4^{3-}$ ,  $\text{NpO}_2(\text{OH})_4^{2-}$ , and  $\text{NpO}_4(\text{OH})_2^{3-}$  are the dominant species of Np(V, VI, VII) in the absence of complexing anions<sup>4)</sup>. The  $E^\circ$  values for Np(VI/V) and Np(VII/VI) in these media are +0.106V and +0.450V. The irreversible reduction of Np(V) to  $\text{NpO}_2$  appears to begin at  $E^\circ = -0.15$  V.

Figure 1 The Fourier Transform (FT) of the U  $L_{II}$  edge EXAFS Spectra in Hanford sludge simulants.



Results of electrochemical experiments in mixed media support the observations of Neck et al.<sup>5)</sup> that mixed mononuclear hydroxycarbonates dominate the speciation of Np(V) and Np(VI). In fact, our electrochemical results suggest that the Np(V) and Np(VI) species are probably isostructural. Np(VII) does not appear to interact significantly with  $\text{CO}_3^{2-}$  at concentrations below 0.3 M total carbonate, as evidenced by the electrochemically irreversible cyclic voltammogram for the Np(VI/VII) couple. At base concentrations above 6 M (in the presence of 0.3 M carbonate), the hydroxide species noted above again appear to dominate the speciation of Np(V, VI, and VII). Recent results indicate that similar speciation patterns are observed for Pu, though higher concentrations of base are required to stabilize Pu(VII).

## V. Conclusions:

In the ongoing first stage of this project we have developed a number of correlations and fresh insights into the nature of the interactions between actinides, alkaline tanks sludges, and reagents that could be used for sludge scrubbing. Comparatively little Pu or Am dissolves from any sludge type as a consequence of the baseline alkaline scrub, but 10-30% of radiotracer U and Np can be mobilized from PUREX sludge into the 3.0 M NaOH. More aggressive sludge leaching protocols indicate that many of the actinides are associated with Fe, Cr, and Mn oxides in the sludges. Oxidative leaching appears to enhance dissolution of Am, strongly suggesting that oxidative leachants will tend to mobilize Np and Pu. Aluminum species are difficult to dissolve from all waste types, at least for leaching at ambient temperatures. There are some indications that Pu can be mobilized on aluminum colloids and that U(VI) dissolution may be associated with Al removal. In concentrated alkali, the dominant species of Np(V) and Np(VI) (and by analogy those of Pu and U) are mononuclear tetrahydroxides whose solubility is somewhat retarded by the presence of  $\text{Na}^+$ . In the solid state, U(VI) species are different in the different sludge simulants.

Where meaningful comparisons can be made to leaching studies of actual sludge samples, these results are consistent with those of the parallel investigations. Overall, our results indicate that actinide ions will behave as expected under most conditions during alkaline sludge washing, but that removal of Al and Cr to adequate levels with the comparatively simple treatment of caustic scrubbing is not likely to succeed. More aggressive protocols to remove these species could have a negative impact on actinide sequestration in the sludge layer. Additional research is required to address these issues.

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